Tuning the thiolen: Al(III) and Fe(III) thiolen complexes for the isoselective ROP of *rac*-lactide

Jack A. Stewart,[§] *Paul McKeown,*[§] *Oliver J. Driscoll,*[§] *Mary F. Mahon,*[§] *Benjamin D. Ward,*[‡] *and Matthew D. Jones*[§,*]

[§]Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK.

[‡]Department of Chemistry, Cardiff University, Park Place, Cardiff, CF10 3AT, UK.

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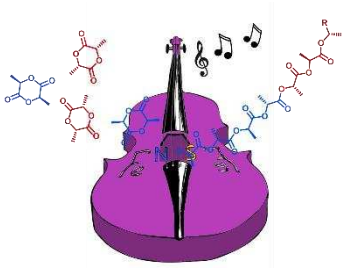


ABSTRACT. A series of five iron and aluminum complexes bearing {ONSO} imine thiobis(phenolate) ligands have been prepared and applied to the ROP of *rac*-lactide. Fe(**1**)Cl produced PLA with a very strong isotactic bias (P_m = 0.79 – 0.89) and well-defined melting temperatures (T_m = 154 – 181 °C). The polymers have been characterized by a combination of $^1H\{^1H\}$ NMR, $^{13}C\{^1H\}$ NMR, GPC, TGA, DSC and pXRD. Fe(**1**)Cl has also been shown to activate CO_2, at atmospheric pressure and concentrations, to form a carbonato bridged dimer. Fe(**2**-**5**)Cl and Al(**1**-**5**)Me were also active for lactide ROP demonstrating good molecular weight control

(Đ = 1.04 – 1.12) and moderate isotactic preference (P_m = 0.56 – 0.72), with polymerization outcome correlating with ligand substituents.

INTRODUCTION

The development of sustainable alternatives to petroleum-based plastics is one of the key scientific challenges of the 21st century. This new generation of bio-derived polymers should be: sourced from annually renewable feedstocks, have properties that can compete with traditional plastics and be easily degradable or reusable, allowing for a "closed-loop" lifecycle.[1] Polylactide (PLA) is an important example of this class of polymers. It is already established as a packaging material[2] and has found use in specialized medical applications due to its biocompatibility.[3-4] Furthermore, it is made from starch feedstocks and is amenable to enzymatic biodegradation[5] or chemical recycling.[6] The most prevalent synthetic route to PLA is through the ring opening polymerization (ROP) of lactide (LA).[7] PLA formed exclusively from the *L* stereoisomer (PLLA) is the current industrial standard, however, the thermal properties can be improved through the stereoselective polymerization of *rac*-LA to form isotactic stereoblock or stereocomplexed PLA.[8] The search for robust, isoselective initiators for the ROP of *rac*-LA is therefore a key aspect of research in this field. There are examples of initiators based on Lewis acidic metals that produce isotactic PLA. These include: Na(I)/K(I),[9–12] Mg(II),[13,14] Ti(IV),[15] Zr(IV)/Hf(IV),[16–22] Zn(II),[23–30] Y(III),[31–35]Al(III)[36–49] and In(III).[50–53] The exact reasons why certain ligand-metal combinations offer high selectivity is still a matter of great academic and industrial interest.[54]

Aluminum initiators have been particularly successful for the isoselective ROP of *rac*-LA.[36–47] Aluminum salen complexes have been shown to produce PLA with a strong isotactic bias that can originate from either achiral or chiral ligand systems.[36–39,42–44] Salan,[40,41,55] half-salan[45] and salalen[46–48] aluminum complexes have also been reported for the production of isotactic PLA. One

disadvantage of aluminum systems is their relatively low activity with several days often required to reach high conversion,[48] although there have been recent reports of room temperature production of PLA using Al systems by Romain and co-workers.[56]

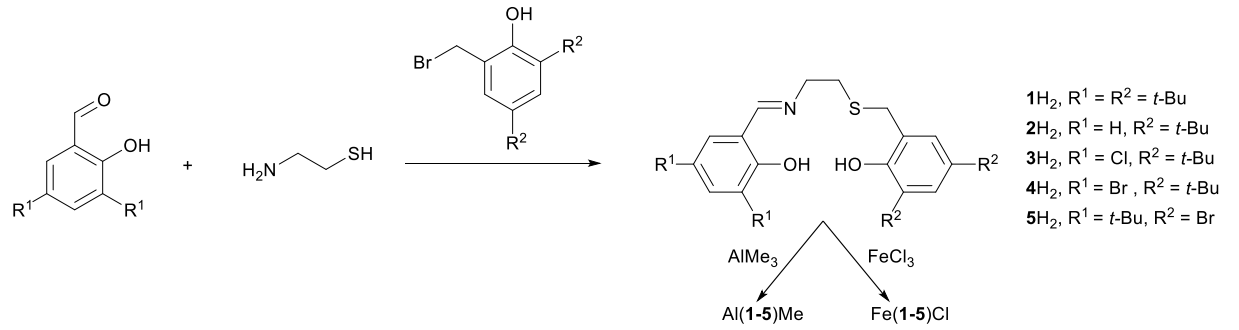
Initiators based on iron have many attractive properties including excellent biocompatibility, low toxicity and very high natural abundance.[57] Despite this, there are only a few reported examples of iron mediated ROP of lactide, especially regarding iron (III) complexes.[58–66] Early studies demonstrated the use of simple ferric alkoxides which showed good activity for lactide ROP with good molecular weight control both in the melt[65] and in toluene at 70 °C.[67] A bis(imino)pyridine iron alkoxide complex was employed by Byers and co-workers who developed a Fe(II)/Fe(III) switchable system that could selectively initiate the ROP lactide or cyclohexene oxide depending on the oxidation state of iron.[63,64] Iron complexes based on [ONO] ligands have exhibited high activity for *L*-LA polymerization both in mononuclear[62] and dinuclear[60] forms. Duan and co-workers reported a series of iron(III) salen complexes that were able to produce PLA with a moderate isotactic bias (P_m < 0.78).[61,66] We recently reported iron(III) salalens that were applied to *rac*-LA polymerization and was shown to have lower activity but better stereocontrol than the analogous salen complex (P_m = 0.80).[58] We also reported an initiation period related to the formation of the active complex from propylene oxide (PO) and this is suggested to account for the long reaction times observed with iron chloride complexes. This corroborates the work of Lamberti and co-workers who did not observe ROP of lactide after four hours with an iron (III) salalen complex.[68] Fe(II) initiators have also been successfully applied to *rac*-LA ROP including recent work by Marin and co-workers who produced highly isotactic stereocomplexed PLA ($P_m \leq$ 0.92, $T_m \leq$ 195 °C) using achiral Fe(II) complexes.[69]

Tetradentate bisphenolate ligands are used for many catalytic transformations and are ubiquitous throughout LA polymerization chemistry.[70] These are typically [ONNO] donors, however, the use of a soft, second row donor can be advantageous to catalytic activity through regulating the Lewis acidity at the metal centre.[71] Okuda and co-workers have reported [OSSO] dithiobisphenolate complexes for both group 3[72] and group 4 metals.[73] These complexes were all active for the ROP of *rac*-LA and tended to have a heterotactic bias ($P_r = 0.66$). Kol and co-workers presented a series of [ONSO] imine-thiobisphenolate ligands with an ethylene bridge.[74] The degree of fluxionality within the complexes was highlighted and the tacticity of the polymer could be varied from isotactic ($P_m = 0.67$) to heterotactic ($P_m = 0.28$) as the rigidity was altered. A similar effect was observed with a phenylene bridged analogue, however the tacticity could only be varied between heterotactic and atactic with the phenolate substituents being the key factor.[75]

Herein, we present a series of imine thiobis(phenolate) ligands complexed to iron (III) and aluminum (III) to provide a comparison between the two metal centres. The former constitutes the most isoselective Fe(III) initiators to date. The ligand substituents are altered in order to probe structure activity relationships through variation of the sterics and electronics of the complexes. This includes the isomeric pair **4**H_2/**5**H_2 in which the effect of altering the imine and thio-ether phenolate substituents are explored. Interestingly, recrystallization of Fe(**1**)Cl yielded both an oxy-bridged and a carbonato-bridged crystal structure. It is suggested that the latter represents an intermediate in the halide-free CO_2/epoxide coupling reaction, as theorized by Müller and coworkers.[76]

RESULTS AND DISCUSSION

Ligand and complex preparation. A series of five ONSO thiolen ligands were prepared containing a combination of electron withdrawing and bulky *tert*-butyl phenolate substituents, Scheme 1. Of these, two (**1**H_2/**3**H_2) were based on literature examples[74] and three (**2**H_2/**4**H_2/**5**H_2) are reported for the first time. All ligands were complexed to iron (III) chloride, in toluene, in the presence of triethylamine. After purification (see Supporting Information for details) the identity of product was confirmed by High-Resolution Mass-Spectrometry (HR-MS). Ions of the form $[Fe(\mathbf{1}\text{-}\mathbf{5})]^+$ were observed, thus confirming ligand coordination to the metal center. Elemental analyses of the iron (III) complexes were consistent with the chloride complexes. Upon recrystallization from dry hexane, a crystal structure of Fe(**1**)Cl was obtained, Fig. 1. The complex tended towards a trigonal bipyramidal geometry (τ_5 = 0.78, Table 1).[77] This preference exceeded that of the corresponding salalen (τ_5 = 0.66, Table 1).[58] The axial axis is occupied by O(2) and S(1) and deviates from the ideal 180° angle as would be expected from the distorted trigonal bipyramidal geometry {O(2)−Fe(1)−S(1) = 166.82(7)°}. The bond angle between Fe(1)−O(1) and Fe(1)−N(1) is the largest equatorial angle and is in close agreement to the ideal value for the proposed geometry {120.24(10)°}. The main point of difference is that the Fe−S(1) bond in Fe(**1**)Cl is considerably longer {2.6220(8) Å} compared to the Fe−N(1) {2.300(2) Å} bond in the respective salalen. The magnetic susceptibility was measured for Fe(**1**)Cl using the Evans NMR method and a Gouy balance, the results of which were indicative of a high spin Fe(III) complex.



Scheme 1. Ligands and complexes used in this study.

During attempts to recrystallize Fe(**1**)Cl, two interesting dimeric structures were obtained. The first, $[Fe(\mathbf{1})]_2O$, (Fig. SI 51) represents a μ-oxo bridged complex and the second, $[Fe(\mathbf{1})]_2CO_3$, Fig. 2 shows a carbonato bridged complex. The sequence Fe(**1**)Cl – Fe(**1**)OH – $[Fe(\mathbf{1})]_2O$ – $[Fe(\mathbf{1})]_2CO_3$ must result from the incorporation of oxygen from serendipitous water, followed by the activation of atmospheric CO_2. This is the first solid-state structural evidence of the insertion of CO_2 into an M-O-M bond with a salen-type ligand. The μ_2–coordination mode corresponds with one of the CO_2 insertion products theorized by Müller and co-workers.[76]

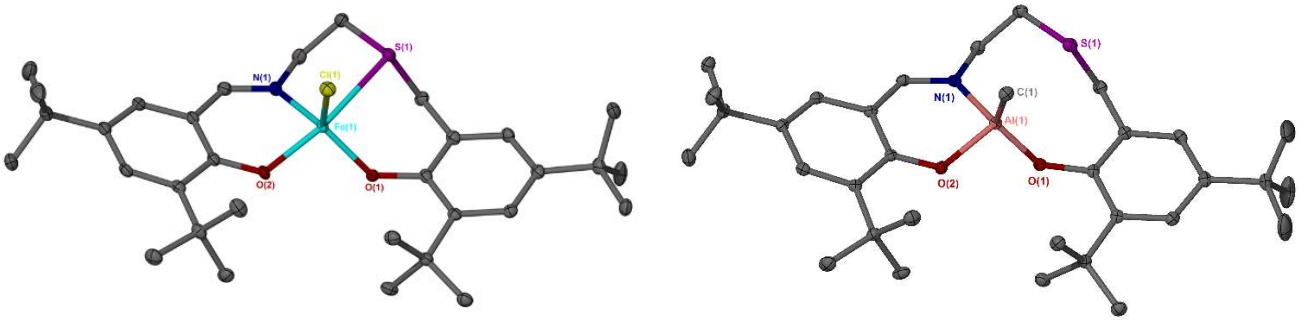


Figure 1. Solid state structures of Fe(**1**)Cl (left) and Al(**1**)Me (right). Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been removed for clarity.

Table 1 Selected bond lengths [Å] and angles [°] Fe{salalen}Cl,[58] Fe(**1**)Cl, Al(**1,2,5**)Me and Al(**1**)Cl.

	Fe{**salalen**}Cl	Fe(**1**)Cl	Al(**1**)Me	Al(**2**)Me	Al(**5**)Me	Al(**1**)Cl
τ_5	0.66	0.78	-	-	-	0.83
τ_4'	-	-	0.91	0.94	0.90	-
M−O(1)	1.8445(16)	1.851(2)	1.7490(17)	1.7048(9)	1.747(2)	1.733(2)
M−O(2)	1.9081(18)	1.9065(18)	1.7990(18)	1.7593(10)	1.780(2)	1.788(2)
M−N(1)	2.047(2)	2.065(3)	1.975(2)	1.9403(12)	1.959(2)	1.951(2)
M−S(1)	-	2.6220(8)	-	-	-	2.6863(11)
M−N(2)	2.300(2)	-	-	-	-	-
M−X	2.2432(7)	2.2367(9)	1.958(2)	1.9415(15)	1.941(3)	2.1652(11)
O(1)−M−N(1)	117.14(8)	120.24(10)	111.57(8)	108.34(5)	108.27(11)	121.11(11)
O(2)−M−S(1)	-	166.82(7)	-	-	-	170.80(8)
O(2)−M−X	-	98.91(7)	102.85(10)	114.38(6)	109.46(14)	99.18(8)
N(1)−M−S(1)	-	79.55(7)	-	-	-	85.40(7)
N(1)−M−X	124.94(6)	116.95(8)	117.03(10)	111.05(7)	119.57(14)	114.86(8)

Ligands **1**-**5**H_2 were complexed to aluminum to give the alkyl complexes Al(**1**-**5**)Me (see Supporting Information for details). These complexes were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy in addition to elemental analysis, which were consistent with monomeric methyl complexes. Solid-state structures of complexes Al(**1**,**2**,**5**)Me were obtained and in all cases a four-coordinate geometry with S(1) uncoordinated was observed. For Al(**1**)Me, the Al(1)–S(1) distance is 2.879 Å which is greater than the sum of the van der Waals radii, implying that there is no bonding interaction. The geometric preference for a four-coordinate complex, τ_4', was calculated.[78] In all cases, a strong preference for tetrahedral geometry was observed (τ_4' = 0.90 –

0.94). This was most pronounced for Al(**2**)Me (R^1 = H, R^2 = *t*-Bu) and can be attributed to a reduced steric hindrance allowing a close adherence to the ideal tetrahedral geometry (τ_4' = 0.94). The Al-related bond angles for Al(**2**)Me are all close to the ideal tetrahedral value {108.34(6)° – 114.38(6)°}. The ^{1}H NMR (298 K, C_6D_6) spectra of Al(**1**-**5**)Me all showed clear resonances at around δ = – 0.15 ppm for the Al-Me moiety.

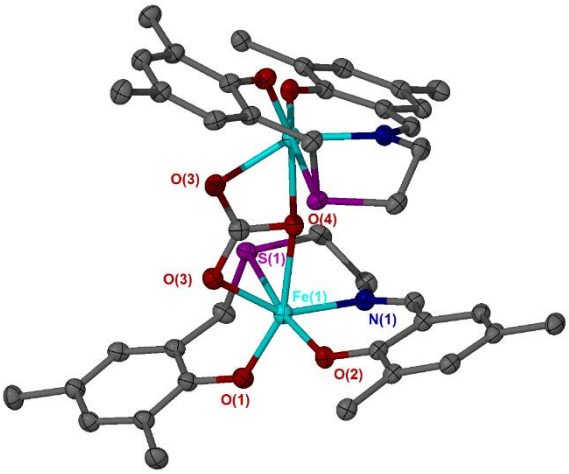


Figure 2. Solid state structure of [Fe(**1**)]$_2$CO$_3$. Ellipsoids are shown at the 30% probability level. Hydrogen atoms and methyl *t*-Bu carbons have been removed for clarity.

The aluminum chloride complex Al(**1**)Cl was synthesized to provide an analogue of Fe(**1**)Cl where the activation with Et_3N and BnOH could be studied using ^{1}H NMR spectroscopy. Unlike with Al(**1**)Me, the sulfur is coordinated to the metal center resulting in a 5-coordinate complex with a distorted trigonal bipyramidal geometry. When BnOH was added to Al(**1**)Cl, two doublets appear at δ = 4.7 and 5.6 ppm corresponding to the BnOH -CH_2- protons alongside a signal for the hydroxyl proton. This is suggestive of a coordinated molecule of BnOH. When Et_3N is added, the aforementioned resonances are replaced by one broad signal at 5.2 ppm, indicative of the formation of an Al–O bond. This implies that Et_3N is required for the formation of the active alkoxide species.

Polymerization. The polymerization of *rac*-LA with Fe(**1**)Cl was initially carried out in 2 mL of purified propylene oxide (PO) at a ratio of 100:1 [LA]:[Fe], Table 2. PO has been previously demonstrated to act as both solvent and co-initiator for iron(III) salen, salan and salalen complexes for *rac*-LA polymerization.[58,61,66,68] At 80 °C, a conversion of 76% was achieved after 24 hours and the resulting polymer was isotactically enriched (P_m = 0.81). A bimodal GPC trace was observed with a broad dispersity and high molecular weight relative to the theoretical value (M_n = 15550 Da, $M_{n,\,theo}$ = 11050 Da, Đ = 1.31). The bimodality can be attributed to a separate initiation with diol impurities present in PO as we have previously reported.[58] Under these conditions, no conversion was observed after six hours. This implies a long initiation period, similar to that observed for other Fe(III) complexes, in PO. [58,68]

Subsequent polymerizations were performed in toluene in the presence of benzyl alcohol as a co-initiator and triethylamine to facilitate the abstraction of the chloride thus generating a classical alkoxide initiating group (100:1:1:1 [LA]:[Fe]:[BnOH]:[Et_3N]). Under the same conditions tested with PO (80 °C, 24 h), conversion was increased to 96% and a moderate improvement in molecular weight control was observed. A polymerization time of four hours resulted in 79% conversion with close agreement between measured and calculated molecular weights as well as a narrow dispersity (M_n = 10500 Da, $M_{n,\,theo}$ = 11500, Đ = 1.04). MALDI-ToF analysis of the polymer (Fig. SI 34) gave a symmetrical distribution with a repeating unit of 144 g mol^{-1} and the expected BnO- + H- end groups. This demonstrates a lack of transesterification processes. The stereoselectivity of the initiator could be improved by lowering the temperature to 50 °C (P_m = 0.84, Table 2, entry 4), although an extended reaction time of 48 hours was required. When the reaction was carried out at 40 °C for 96 h, stereocontrol was increased as shown by $^1H\{^1H\}$ NMR (P_m = 0.85) and $^{13}C\{^1H\}$ NMR (Fig. SI 33).

Table 2. ROP of *rac*-LA with Fe(**1-5**)Cl

Entry	Init.	T/°C	Time /hours	Conv. %[a]	P_m[b]	M_n Calc.[c]	M_n[d]	Đ[d]	T_m
1	Fe(**1**)Cl[e]	80	24	76	0.81	11050	15550	1.31	154
2	Fe(**1**)Cl	80	24	96	0.79	13950	9400	1.15	-[g]
3	Fe(**1**)Cl	80	4	79	0.79	11500	10500	1.04	170
4	Fe(**1**)Cl	50	48	95	0.84	13800	13500	1.04	174
5	Fe(**1**)Cl	40	96	96	0.85	13950	11350	1.51	177
6	Fe(**1**)Cl	40	48	82	0.84	11900	14300	1.44	174
7	Fe(**1**)Cl[f]	40	48	88	0.89	12800	16500	1.19	181
8	Fe(**2**)Cl	80	2	88	0.57	12800	9500	1.11	-[g]
9	Fe(**3**)Cl	80	1	79	0.61	11500	7600	1.04	-[g]
10	Fe(**4**)Cl	80	0.5	93	0.62	13500	5750	1.08	-[g]
11	Fe(**5**)Cl	80	3	83	0.71	12050	7950	1.04	-[g]

Conditions: *rac*-LA (0.4 g), [LA]:[Fe]:[BnOH]:[Et_3N] = 100:1:1:1 unless otherwise stated; [a] Determined by ^1H NMR spectroscopy; [b] Probability of isotactic enchainment, determined by $^1H\{^1H\}$ NMR spectroscopy; [c] Theoretical molecular weight calculated from conversion (rounded to the nearest 50): {[LA]:[I] × (Conversion × 144.13) / BnOH equiv.} + M_n (BnOH); [d] Determined from GPC (in THF) referenced against polystyrene standards, × 0.58; [e] [LA]:[Fe] = 100:1, PO (2 ml); [f] stirred at 80 °C for 4 hours prior to addition of *rac*-LA. [g] not determined.

For this polymer, a bimodal GPC trace was obtained with a relatively broad dispersity (Đ = 1.51). This could suggest a competitive reaction mechanism, such as activated monomer, which has been observed competing at low temperatures with the more common coordination-insertion mechanism.[27] MALDI-ToF mass spectrometry (Fig. SI 40) shows a low M_n series (M_p = 5032 Da) only, presumably this ionises more readily than the higher M_n series; the M_p corresponds to the

low molecular weight portion determined from GPC deconvolution (Fig. SI 46). Reducing the reaction time to 48 h slightly lowered the dispersity (Đ = 1.44) suggesting that the extended reaction time is only a minor contribution to the bimodality. It is suggested that 40 °C is not sufficient to completely displace the Cl and form the alkoxide, thus promoting activated monomer reactivity. To examine this, the complex was "pre-activated" with BnOH and Et_3N at 80 °C for four hours before the addition of LA and subsequent polymerization at 40 °C. This resulted in a narrow dispersity (Đ = 1.19) and improved stereocontrol (P_m = 0.89) alongside a small increase in conversion. These results are consistent with the suppression of an activated monomer mechanism in favor of coordination-insertion. The high P_m associated with this experiment was corroborated by $^{13}C\{^1H\}$ NMR of the methine region (Fig. SI 32). A polymerization was also attempted without the addition of NEt_3 ([LA]:[Fe]:[BnOH] 100:1:1) in this case after 3 hrs at 80 °C an 80% conversion was achieved, P_m was lower 0.76 (*c.f.* 0.79 with Et_3N), with M_n = 12500 Da and Đ = 1.04. From NMR spectroscopic studies with Al(**1**)Cl studies we hypothesised that the addition of Et_3N was necessary to facilitate the formation of the alkoxide, hence for the polymerization without Et_3N an activated monomer is likely to be in operation and with Et_3N the mechanism is the classical coordination insertion.

The most isotactic polymers were subjected to further characterization to assess their thermal properties and crystallinity. pXRD of a polymer example (Table 2 entry 5) demonstrated sharp peaks that are indicative of a crystalline polymer (Fig. SI 50). The decomposition properties of the same polymer were analysed through TGA (Fig. SI 48). From the decomposition profile it can be seen that the polymer begins to degrade at around 215 °C and reaches full decomposition at 308 °C, in accordance with previously reported values for isotactic stereocomplexed PLA.[69] This data was used to set the parameters for the DSC so as to avoid decomposition of the samples after the

first heating cycle. Melting points were obtained for six polymer samples (Fig. SI 49) with the highest (T_m = 181°C) corresponding to the highest isotacticity as measured through $^1H\{^1H\}$ NMR (P_m = 0.89). For the other samples, a higher melting point is associated with a higher P_m value as would be expected of isotactic stereocomplex PLA. The exception is the polymer initiated with PO which has a significantly lower melting point than would be expected (T_m = 154 °C, P_m = 0.81).

The less sterically hindered complex Fe(**2**)Cl (R^1 = H, R^2 = *t*-Bu) was more active than Fe(**1**)Cl achieving high conversion after two hours at 80 °C. However, this activity comes at the expense of stereoselectivity and the resulting PLA was essentially atactic (P_m = 0.57). Halogenated analogues Fe(**3**)Cl (R^1 = Cl, R^2 = *t*-Bu) and Fe(**4**)Cl (R^1 = Br, R^2 = *t*-Bu) achieved high conversion after one hour and 30 minutes respectively. This increase in activity can be attributed to an increase in Lewis acidity at the Fe center brought about by the electron withdrawing substituents.[79] The isotactic bias was slightly higher than with Fe(**2**)Cl likely as a result of the steric bulk of the halides. Fe(**2-4**)Cl produced PLA with narrow dispersities (Đ = 1.04 – 1.11) although molecular weights obtained were lower than the theoretical values. MALDI-ToF analysis of the polymers produced by Fe(**2-4**)Cl shows consistently symmetrical distributions with no transesterification and the expected BnO- + H- end groups throughout.

The isomeric pair of Fe(**4**)Cl (R^1 = Br, R^2 = *t*-Bu) and Fe(**5**)Cl (R^1 = *t-Bu*, R^2 = Br) were prepared to investigate the effect of altering the substituents on the imino-phenolate and thio-phenolate side of the ligand. Fe(**5**)Cl was less active than Fe(**4**)Cl achieving high conversion after a three hour reaction time. It did, however, produce a more controlled polymer in terms of dispersity and the agreement between theoretical and experimental molecular weights. Additionally, the polymer produced by Fe(**5**)Cl was more isotactic (P_m = 0.71) than by Fe(**4**)Cl (P_m = 0.62). The fast reaction

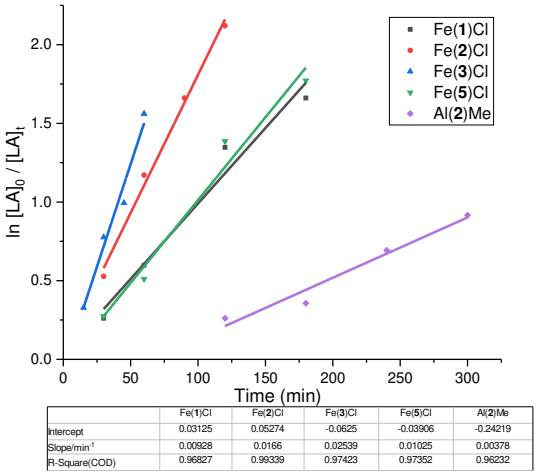
time of Fe(**4**)Cl could account for the lack of ROP control, with some polymer degradation occurring at high conversion. In comparison with Fe(**1**)Cl, it appears that altering the imine-phenolate moiety has a dramatic effect on the ROP of lactide with significantly increased activity coming at the expense of control and stereoselectivity. The same alteration to the thio-phenolate reduced ROP control but did not increase the activity of the initiator.

Al(**1**-**5**)Me were applied to *rac*-LA polymerization in toluene with the addition of benzyl alcohol for the *in situ* generation of the active alkoxide species, Table 3. Al(**1**)Me ($R^1 = R^2 = t$-Bu) could only achieve 22% conversion after 48 hours and a reaction time of 240 hours was ultimately required to achieve high conversion. The stereocontrol ($P_m = 0.69$) was reduced compared to the analogous Fe(III) complex and a broader dispersity was observed (Đ = 1.12), likely as a result of extended reaction time. Al(**2**-**4**)Me were more active each giving reasonable conversion after five hours. As with Fe(III) initiators, the halogenated analogues were more active than the unsubstituted thiolen complex. The polymers produced from Al(**2**-**4**)Me had narrow dispersities (Đ = 1.05 – 1.06) although the molecular weights were all below the theoretical values and only a slight isoselectivity was observed. MALDI-ToF analysis of the polymer produced by Al(**2**)Me (Fig. SI 39) showed a single series with a repeat unit of 72 Da, indicating a high degree of transesterification. When the thio-phenolate substituents were altered {Al(**5**)Me, $R^1 = t$-Bu, R^2 = Br} an increase in selectivity was observed ($P_m = 0.72$) however the activity was reduced giving high conversion after 72 hours. This again mirrors the trend observed with Fe(**1**-**5**)Cl. The polymer initiated by Al(**5**)Me gave three separate series in the MALDI-ToF spectrum corresponding to linear polymer, transesterified polymer and a separate ionization event with potassium.

Table 3. ROP of *rac*-LA with Al(**1**-**5**)Me.

Init.	T/°C	Time /hours	Conv. %[a]	P_m[b]	M_n Calc.[c]	M_n[d]	Đ[d]
Al(**1**)Me	80	48	22	0.64	3300	-	-
Al(**1**)Me	80	240	92	0.69	13350	9800	1.12
Al(**2**)Me	80	5	60	0.56	8750	6350	1.06
Al(**3**)Me	80	5	69	0.58	10050	6650	1.06
Al(**4**)Me	80	5	72	0.58	10500	7600	1.05
Al(**5**)Me	80	72	84	0.72	12200	4750	1.09

Conditions: *rac*-LA (0.4 g), [LA]:[Al]:[BnOH] = 100:1:1; [a] Determined by ^{1}H NMR spectroscopy; [b] Probability of isotactic enchainment, determined by ^{1}H{^{1}H} NMR spectroscopy; [c] Theoretical molecular weight calculated from conversion (rounded to the nearest 50): {[LA]:[I] × (Conversion × 144.13) / BnOH equiv.} + M_n (BnOH). # [d] Determined from GPC (in THF) referenced against polystyrene standards, × 0.58 (rounded to the nearest 50).



	Fe(1)Cl	Fe(2)Cl	Fe(3)Cl	Fe(5)Cl	Al(2)Me
Intercept	0.03125	0.05274	-0.0625	-0.03906	-0.24219
Slope/min^{-1}	0.00928	0.0166	0.02539	0.01025	0.00378
R-Square(COD)	0.96827	0.99339	0.97423	0.97352	0.96232

Figure 3. Semi-logarithmic plot of ROP of *rac*-LA with Fe(**1**,**2**,**3**,**5**) and Al(**2**)Me.

Kinetic Studies. Batch kinetics were carried out for Fe(**1**,**2**,**3**,**5**)Cl and Al(**2**)Me, Fig. 3. Fe(**4**)Cl was too active to produce comparable kinetics with the other initiators. The fitted lines for the Fe(III) complexes intercept close to zero whereas Al(**2**)Me gives a non-zero intercept indicative of an induction period to generate the alkoxide. This fits with the lengthy reaction times required during ROP with Al(III) complexes. For all complexes, LA is consumed with a first-order dependence. The highest rate is observed with Fe(**3**)Cl (k_{app} = 0.025 min^{-1}, R^2 = 0.97) as may be expected by the electron-withdrawing substituents making the Fe (III) center more electron-deficient. This can also account for the high activity of Fe(**4**)Cl. Fe(**2**)Cl has the next highest rate (k_{app} = 0.017 min^{-1}, R^2 = 0.99) presumably due to reduced steric bulk. Fe(**1**)Cl (k_{app} = 0.009 min^{-1}, R^2 = 0.97) is faster than the analogous Fe(III) salalen[58] and has a very similar rate to Fe(**5**)Cl (k_{app} = 0.010 min^{-1}, R^2 = 0.97) suggesting that altering the thio-phenolate substituents have little impact on the rate of reaction. Al(**2**)Me was slower than Fe(**1**-**5**)Cl (k_{app} = 0.003 min^{-1}, R^2 = 0.96) but does compare favorably with the activity of ethylene bridge salalens.[79] For Fe(**1**)Cl, a linear

relationship between molecular weight and conversion is demonstrated, Fig. 4, which is good evidence of a "living" polymerization. The plot also shows that P_m remains consistent after the first point and that a very narrow dispersity is maintained throughout the reaction.

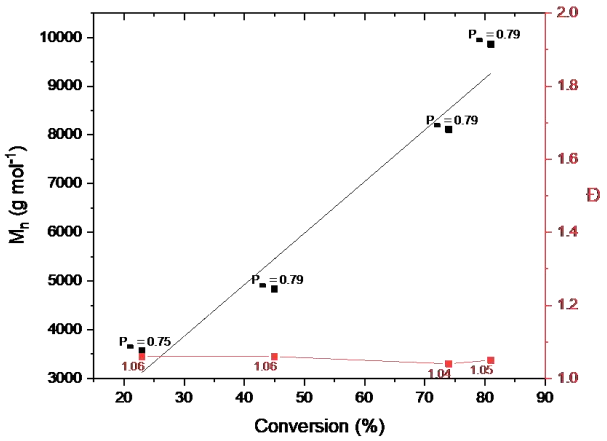


Figure 4. M_n vs. conversion plot for Fe(**1**)Cl, T = 80 °C.

CONCLUSION

Five thiolen ligands have been complexed to iron and aluminum and the resultant complexes were characterized through combinations of mass spectrometry, NMR spectroscopy, elemental analysis and, where possible, X-ray crystallography. The solid-state structure of Fe(**1**)Cl was five coordinate with a tendency towards a trigonal bipyramidal geometry (τ_5 = 0.78). The structures of Al(**1**,**2**,**5**)Me were four coordinate in the solid-state with no aluminum-to-sulfur bond and a strong preference for tetrahedral geometry (τ_4, = 0.90 – 0.94). All complexes were active towards the ROP of *rac*-LA with varying degrees of activity and stereoselectivity. Fe(**1**)Cl produced highly isotactic PLA which was shown to be crystalline and have defined melting temperatures (T_m = 154 – 181 °C). At low temperature, evidence was presented for an activated monomer mechanism in competition with the typical coordination-insertion pathway. Reducing the steric bulk of the ligands and the introduction of electron-withdrawing substituents resulted in higher activity at the

expense of stereocontrol. The ROP initiated by Al(**1**-**5**)Me was significantly slower and less selective than Fe(III) complexes but maintained good molecular weight control.

ASSOCIATED CONTENT

Supporting Information

The Electronic Supplementary Information (ESI) is available free of charge.

Full experimental details and methods, ligand and NMR spectra, polymer characterization, and X-ray details. (PDF)

AUTHOR INFORMATION

Corresponding Author

* Fax: +44 (0) 122 538 6231. Tel.: +44 (0) 122 538 4908. E-mail:mj205@bath.ac.uk

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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